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(54) Title: POLYESTER STAPLE FIBERS AND METHOD FOR THE PRODUCTION THEREOF

(57) Abstract: Polyester staple fibers consisting of a polyester, 0.1 to 2.0 w.- % of an incompatible, melt processable, amorphous polymeric additive with a glass transition temperature of 90 to 170 °C and a melt viscosity/polyester component ratio of 1:1 to 10:1, and 0 to 5.0 weight % of usual additives. The polymeric additives in the staple fibers are present in the form of fibrils with a mean diameter of ≤ 80 nm. The invention also relates to method for the production of staple fibers, comprising mixing and simultaneously shearing the polyesters and the polymeric additives and optionally the usual additives and spinning at a speed of < 2500 m/min relative to form of spun fibers. Said are bundled together to form cables and stretched in aseparate drawframe to form separate reels of fiber, crimped, dried and cut to form staple fibers.

Polyester Staple Fibers and Method for the Production Thereof

Description:

The invention relates to polyester staple fibers and a method for the production of these staple fibers.

Staple fibers, made of polyethylene terephthalate, and a method for the production thereof have been known for a long time (F. Fourné, Synthetic Fibers, Hanser Publishers, Munich [1995] pp. 91 - 94 and pp. 462 - 486).

In addition to the quality of the staple fibers, the spinning factor SF, that is the throughput (g/min) per spinneret hole field area (cm^2), is important, where

$$SF = LD \cdot d \cdot VV \cdot v \cdot 10^{-4} \cdot K$$

and   LD   hole density (n/cm^2) = the number of spinneret holes per spinneret hole field area,

     d   staple fiber titer (dtex)

     d_0 filament titer (dtex),

     VV   total draw ratio = 1: ...,

     v   rate of haul-off (m/min),

     K   polyester-dependent constant, where

$$K = \frac{d}{(d_0 \cdot VV)} = \frac{(100 - Relax\ (\%)}{100}, \text{ for example}$$

about 0.92 for PET and about 0.73 for PTT.

The object is to achieve the maximum spinning factor, preferably in the range of 2.9 to 10.0.

The hole density LD is specified by the available spinning system and cannot be increased arbitrarily even for geometrical reasons. Due to the tow baling system of the filaments and their further processing into staple fibers, the haul-off rate is limited to speeds below 2,500 m/min. The draw ratio is a function in first approximation of the elongation at break of the filament in a linear correlation, where the higher the rate of haul-off, the lower the elongation at break for a given polymer. Even low titers, especially microfilaments < 1 dpf, or intensive cooling reduce the elongation at break and thus the draw ratio and the spinning factor: capacity losses are the result. Consequently at a specified rate of haul-off the spinning factor can be increased by choosing a polymer with a higher elongation at break. On the other hand, the polymer is indicative for the quality of the staple fibers and, therefore, cannot be changed or can be changed only minimally.

The WO 99-07927 A1 discloses that the elongation at break of pre-oriented polyester filaments (POY), which are spun at haul-off rates of at least 2,500 m/min, preferably at rates between 3,000 and 6,000 m/min, can be increased by adding amorphous, melt processible copolymers, based on styrene, acrylic acid and/or maleic acid or their derivatives, as compared to the elongation at break of polyester filaments, which are spun under the same conditions, without an additive. However, the process cannot be transferred to filaments, produced at haul-off rates of less than 2,500 m/min, because, in contrast to POY fibers, they are not crystalline enough (< 12%) and exhibit a high boiling water shrinkage (> 40%) and a high elongation at break (> 225%).

The EP 0 080 274 B and EP 0 154 425 B achieve the same effect with the addition of polyolefins or PA-66 to polyethylene terephthalate. According to EP 0 080 274 B, the effect increases as the rate of haul-off increases. The take-up speed must amount to at least 2,000 m/min. According to EP 0 154 425 B, the effect can be achieved - even if on a smaller scale - even at lower take-up speeds, provided the polyethylene terephthalate exhibits an intrinsic viscosity of more than 0.70 dl/g.

EP 0 631 638 B describes subsequently end-stretched polyethylene terephthalate threads containing imidized poly(methacrylic alkyl ester). The industrial yarns, spun at 510 m/min, do, in

fact, exhibit a raised elongation at break, but the drawing is not improved; and the yarns also have otherwise worse properties than threads without any additive.

Furthermore, it is known that polypropylene terephthalate (EP 745 711 A, WO 96/000 808 A) and polybutylene terephthalate (US 4 877 572) can be spun into endless filaments. However, there is no statement about their suitability for producing staple fibers.

The object of the present invention is to maximize the spinning factor in the production of polyester staple fibers. The staple fibers must exhibit the same or better quality values than the staple fibers that are produced according to prior art methods.

This problem is solved, according to the invention, with polyester staple fibers and with a method for their production, according to the disclosure in the patent claims.

Polyester is defined as poly(C_{2-4}-alkylene)-terephthalate, which can contain up to 15 Mol-% of other dicarboxylic acids and/or diols, such as isophthalic acid, adipic acid, diethylene glycol, polyethylene glycol, 1,4-cyclohexane dimethanol, or the respectively other C_{2-4}-alkylene glycols. Preferred is polyethylene terephthalate having an intrinsic viscosity (I.V.) ranging from 0.5 to 0.7 dl/g, polypropylene terephthalate having an I.V. ranging from 0.6 to 1.2 dl/g and polybutylene terephthalate having an I.V. ranging from 0.6 to 1.2 dl/g. Typical additives, such as dyes, delustring agents, stabilizers, antistatic agents, lubricants, branching agents, can be added to polyester or the mixture of polyester and additive in quantities ranging from 0 to 5.0 % by wt. without any drawback.

According to the invention, a copolymer is added to the polyester in a quantity ranging from 0.1 to 2.0 % by wt. The copolymer must be amorphous and largely insoluble in the polyester matrix. In essence the two polymers are incompatible with each other and form two phases that can be distinguished under a microscope. Furthermore, the copolymer must have a glass transition temperature (determined by DSC at 10° C / min heating rate) ranging from 90 to 170 deg. C. and must be processible like a thermoplastic material.

The melt viscosity of the copolymer is chosen in such a manner that the ratio of its melt viscosity, which is extrapolated to the zero measurement time and which is measured at an oscillation rate of 2.4 Hz and a temperature, which is equal to the melting temperature of polyester plus 34.0° C (290° C for polyethylene terephthalate) relative to those of polyester, measured under the same conditions, ranges between 1 : 1 and 10 : 1. That is, the melt viscosity of the copolymer is at least the same or preferably higher than that of polyester. The optimal efficiency is not reached until a specific viscosity ratio between additive and polyester is chosen. At such an optimized viscosity ratio, it is possible to minimize the quantity of the additive added. The economic efficiency of the method is especially high; and especially good processing properties are achieved. Surprisingly the ideal viscosity ratio of the invention for the use of polymer mixtures for producing staple fibers is above the range, which has been established in the literature as optimal for mixing together two polymers. Contrary to the state of the art, polymer mixtures having high molecular copolymers could be spun excellently. It has been shown surprisingly that under the conditions, according to the invention, the melt viscosity of the mixture is not noticeably increased. The result is that an increase in pressure losses in the melt lines is positively avoided.

Due to the high flow activation energy of the additive polymers, the viscosity ratio soars in the region, where the filament is formed, after the polymer mixture issues from the spinneret. By choosing a favorable viscosity ratio one obtains an especially narrow particle size distribution of the additive in the polyester matrix; and by combining the viscosity ratio with the flow activation energy of significantly more than that of the polyester (PET about 60 kJ/mol), i.e. of more than 80 kJ/mol, one obtains the fibril structure of the additive in the filament. The higher glass transition temperature compared to that of polyester ensures a rapid stabilization of this fibril structure in the filament. The maximum particle size of the additive polymer directly upon leaving the spinneret nozzle is about 1,000 nm, whereas the mean particle size is 400 nm or less. After drafting below the spinneret, fibrils having a mean diameter of $\leq$ 80 nm are achieved.

Preferably the ratio between the melt viscosity of the copolymer and the polyester under the aforementioned conditions is between 1.5:1 and 7:1. Under these conditions the mean particle

size of the additive polymer directly after leaving the spinneret ranges from 120 to 300 nm; and the results are fibrils having a mean diameter of about 40 nm.

The additive polymers, to be added according to the invention, to the polyester, can exhibit different chemical compositions, provided they have the aforementioned properties. Preferred are three different types of copolymers, namely:

1.   A copolymer, which contains the following monomer units:

A =   acrylic acid, methacrylic acid or $CH_2 = CR - COOR'$, where R is an H atom or a CH_3 group, and R' is a C_{1-15}-alkyl group or a C_{5-12}- cycloalkyl group, or a C_{6-14}-aryl group,
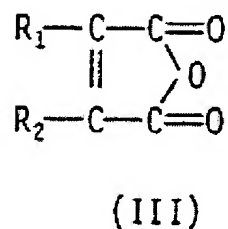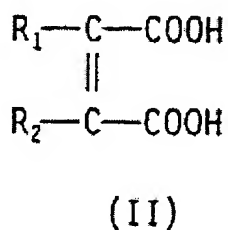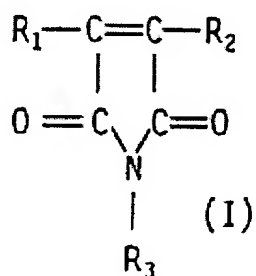
B =   styrene or C_{1-3}-alkyl-substituted styrenes,

where the copolymer comprises 60 to 98 % by wt. of A and 2 to 40 % by wt. of B, preferably comprises 83 to 98 % by wt. of A; and 2 to 17 % by wt. of B, and in particular preferably comprises 90 to 98 % by wt. of A and 2 to 10 % by wt. of B (sum = 100 % by wt.).

2.   A copolymer, which contains the following monomer units:

C =   styrene or C_{1-3}-alkyl-substituted styrenes,

D =   one or more monomers of formula I, II or III

$$
\begin{array}{ccc}
R_1\!-\!C\!=\!C\!-\!R_2 & R_1\!-\!C\!-\!COOH & R_1\!-\!C\!-\!C\!=\!0 \\
\mid \quad \mid & \parallel & \parallel \;\;>\!0 \\
0\!=\!C\;\diagdown\!\diagup\;C\!=\!0 & R_2\!-\!C\!-\!COOH & R_2\!-\!C\!-\!C\!=\!0 \\
N & & \\
\mid \quad (I) & (II) & (III) \\
R_3 & &
\end{array}
$$

where R_1, R_2 and R_3 are each independently an H atom or a C_{1-15}-alkyl group, or a C_{5-12}-cycloalkyl group or a C_{6-14}-aryl group,
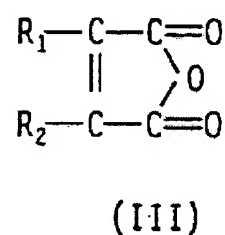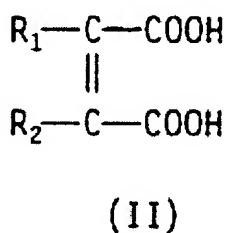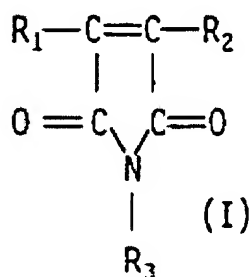
where the copolymer comprises 15 to 95 % by wt. of C and 5 to 85 % by wt. of D; preferably comprises 50 to 90 % by wt. of C and 10 to 50 % by wt. of D; and in particular preferably comprises 70 to 85 % by wt. of C and 15 to 30 % by wt. of D. The sum of C and D together makes 100%.

3.   A copolymer, which contains the following monomer units:

E =   acrylic acid, methacrylic acid or $CH_2 = CR - COOR'$, where R is an H atom or a CH_3 group; and R' is a C_{1-15}-alkyl group or a C_{5-12}-cycloalkyl group, or a C_{6-14}-aryl group,

F =   styrene or C_{1-3}-alkyl-substituted styrenes,

G =   one or more monomers of formula I, II or III

where R_1, R_2 and R_3 are each independently an H atom or a C_{1-15}-alkyl group, or a C_{5-12}-cycloalkyl group or a C_{6-14}-aryl group,

H =   one or more ethylenically unsaturated monomers copolymerizable with E and/or with F and/or with G, selected from the group consisting of alpha-methyl styrene, vinyl acetate, acrylates and methacrylates, which are different from E; vinyl chloride, vinylidene chloride, halogen-substituted styrenes, vinyl esters, isopropenyl ethers and dienes,

where the copolymer comprises 30 to 99 % by wt. of E; and 0 to 50 % by wt. of F; > 0 to 50 % by wt. of G; and 0 to 50% by wt. of H, preferably comprises 45 to 97 % by wt. of E, 0 to 30 % by wt. of F, 3 to 40 % by wt. of G and 0 to 30 % by wt. of H, and in particular preferably comprises 60 to 94 % by wt. of E, 0 to 20 % by wt. of F, 6 to 30 % by wt. of G and 0 to 20 % by wt. of H. The sum of E, F, G and H together makes 100%.

The component H is an optional component. Even though the advantages to be gained with the invention can be achieved with copolymers, which exhibit components selected from the groups E to G, the advantages to be gained with the invention also materialize when other monomers, selected from the group H, participate in the synthesis of the copolymer to be used according to the invention.

The component H is preferably selected in such a manner that it has no negative effect on the properties of the copolymer to be used according to the invention. The component H can be used, among other things, to modify the properties of the copolymer in the desired way, for example by increasing or improving the flow properties, when the copolymer is heated to the melt temperature, or to reduce a residual color in the copolymer or by using a polyfunctional monomer to introduce in this manner a certain degree of cross-linking in the copolymer.

In addition, H can be selected so that a copolymerization of components E to G is possible at all or is aided, as in the case of MSA and MMA, which in themselves do not copolymerize, but with the addition of a third component, like styrene, copolymerize without any problems. Examples of monomers that are suitable for this purpose are, among others, vinyl ester; esters of acrylic acid, for example, methylacrylate and ethyl acrylate; esters of methacrylic acid, which are different from methyl methacrylate, for example, butyl methacrylate and ethyl hexyl methacrylate; vinyl chloride; vinylidene chloride; styrene; alpha-methyl styrene and the various halogen-substituted styrenes; vinyl ether and isopropenyl ether; dienes, such as 1,3-butadiene and divinyl benzene. The color reduction of the copolymer can be achieved, for example, in particular preferably by adding an electron-rich monomer, such as a vinyl ether, vinyl acetate, styrene or alpha-methyl

styrene. Especially preferred among the compounds of the component H are aromatic vinyl monomers, such as styrene or alpha-methyl styrene.

The production of the copolymers, to be used according to the invention, is well-known. They can be produced in the substance, solution, suspension or emulsion polymerization process. Useful instructions regarding substance polymerization can be found in Houben-Weyl, volume E20, part 2 (1987) pp. 1145 ff. Instructions regarding solution polymerization can also be found there on pages 1149 ff, whereas emulsion polymerization is also carried out and explained there on pages 1150 ff.

Especially preferred within the scope of the invention are bead polymerizates, the particle size of which is in a very favorable range. Preferably the copolymers, which are to be used, according to the invention, by mixing, for example, into the melt of the fiber polymers, are present in the form of particles having a mean diameter ranging from 0.1 to 1.0 mm. However, larger or smaller beads or granules can also be used. However, smaller beads impose special requirements on the logistics, like conveying and drying.

The imidized copolymer types 2 and 3 can be produced from monomers by using both a monomer imide and by subsequent complete or preferably partial imidization of a copolymer, containing the corresponding maleic acid derivative. These additive polymers are obtained, for example, by complete or preferably partial reaction of the corresponding copolymer in the melt phase with ammonia or a primary alkyl- or aryl-amine, for example aniline (Encyclopedia of Polymer Science and Engineering, vol. 16 [1989], Wiley Publishers, page 78). All of the inventive copolymers as well as, provided they exist, their non-imidized starting copolymers, are commercially available or can be produced according to a process, with which the person skilled in the art is familiar.

The quantity of the copolymer to be added to the polyester ranges from 0.1 to 2.0 % by wt. Usually a quantity of less than 1.0% of the polymer to be added suffices.

For staple fibers, which exhibit a titer ranging from 0.5 to 4.0 dtex and which were spun at a haul-off rate ranging from 900 to 2,200 m/min, the additive concentration C in % by wt. is chosen in particular preferably in the range of 0.1 to 2.0 % by wt. so that

$$C = \frac{(R_d - R_{do})}{b}$$

where R_{do} is the elongation at break in % of the filament without the additive addition and R_{do} x < R_d; and b = 80 to 160, preferably b = 115 to 152. In this respect R_d, the desired elongation at break of the filament with the additive addition, is $\geq$ 370%, when R_{do} is $\leq$ 354%.

It has been demonstrated surprisingly that the described additive properties of the invention and the resulting special fibril structure in the filament leads to high efficiency. That is, based on the effect that one would like to obtain, the quantity of the additive to be used is very small compared to that of the prior art. The desired effect can be adjusted over a wide range. This property is surprising, because in making the filaments for the production of staple fibers a low spinning orientation, a barely existing crystallization and high boiling water shrinkage values and elongation values generally limit the possibility of achieving profitable or qualitative effects with polymer mixtures. Consequently an increase in the elongation of the filament can often be achieved, but in drawing at the fiber drawframe, inadequate increases in the draw ratio are achieved and the influence on the spinning factor remains insignificant.

To determine the spinning factor it is necessary to know the draw ratio. There is no general rule, because the draw ratio is a function not only of the filament structure, characterized by the elongation at break (Rd) of the filament, but also the desired characteristics of the end product. Nevertheless, a correlation can be approximated in the form of

$$VV = 1 + a \cdot \frac{Rd\ (\%)}{100},$$

where a = 0.48 to 0.96 and preferably a = 0.58 - 0.72 is chosen (for the production of the staple fibers, according to the invention, a is typically, contrary to the prior art, < 1).

Within this range a is chosen in accordance with the desired quality of the staple fibers, so that the result is a low VV for staple fibers having high elongation and a high VV for staple fibers having low elongation at otherwise the same elongation at break R_d of the filament.

After the production of filaments and the breaking elongation test, the associated draw ratio without the addition of the additive can be derived from this formula, where VV = VV_0; and SF can be determined. If at this stage the additive is added in a concentration of C = 0.1 to 2.0%, the draw ratio increases, according to the invention, to $VV = VV_o + \frac{z \bullet C (\%)}{100}$. A desired VV > VV_0 can be set by adding the additive in the range of 0.1 to 2.0 % by wt. in a concentration of $C = \frac{(VV - VV_o)}{z} \bullet 100\%$, where VV $\geq$ VV_0 + 0.153. In this respect Z ranges from 39 to 153.

That is, for a desired increase in the draw ratio VV = VV_0, the concentration C in % is set in the range $\frac{VV - VV_o}{153} \bullet 100 \leq C \leq \frac{VV - VV_o}{39} \bullet 100$.

Thus, an increase in the draw ratio of (VV - VV_0) = 0.20 can be set by adding an additive corresponding to C = 0.14 to 0.51%, and an increase (VV - VV_0) = 0.45 can be set by adding an additive corresponding to C = 0.30 to 1.15%. Preferably Z is chosen between 66 and 146, and an increase in the draw ratio of (VV - VV_0) $\geq$ 0.45 is realized.

In the event that there is a variation in at least one of the variables influencing the spinning factor, the invention makes it possible to compensate in such a manner for any decrease in the draw ratio with the addition of the additive that SF remains at least constant.

Thus, at constant polymer throughput in the spinning system and hence constant SF, the hole density LD can be increased, a feature that leads to a smaller VV, with the result that a desired smaller titer, especially microtiter, can no longer be produced. The addition of the additive increases the VV; and smaller titers can be produced with the same SF. If at constant hole density the titer or the spinning speed is changed, lower VVs can be compensated with the additive; and the SF can be increased in proportion to the throughput of the spinning system.

The mixing of the additive polymer (copolymer) with the matrix polymer is carried out by adding the additive polymer as a solid to the matrix polymer chips in the extruder inlet with chip mixers or by gravimetric metering or as an alternative by melting the additive polymer, metering with a gear pump and feeding into the melt stream of the matrix polymer. Even so-called master batch techniques are possible. In this case the additive exists as a concentrate in the polyester chips, which are added later as a solid or in the molten state to the matrix polyester. Even the addition to a substream of the matrix polymer, which is then admixed to the main stream of the matrix polymer, is practical.

Then a homogeneous distribution through the mixture is produced by means of static mixers. The specific choice of mixer and the duration of the mixing process results advantageously in a defined particle distribution, before the melt mixture is passed through the product distribution line to the individual spinning positions and spinnerets. Mixers having a shear rate ranging from 12 to 128 sec^{-1} have given satisfactory results. In so doing, the product from a shear rate (sec^{-1}) and the 0.8th power of the dwell time (in sec.) should amount to at least 250, preferably 350 to 1,250. Values above 2,500 are generally avoided to keep the pressure drop in the pipelines within limits.

In this respect the shear rate is defined by the shear rate in the empty pipe (sec^{-1}) times the mixer factor, where the mixer factor is a characteristic statistic of the type of mixer. For Sulzer-SMXL models, for example, this factor ranges from about 3.5 - 4. The shear rate γ in the empty pipe is calculated according to

$$\gamma = \frac{4 \cdot 10^3 \cdot F}{\pi \cdot \delta \cdot R^3 \cdot 60} \left[s^{-1} \right]$$

and the dwell time t (s) according to

$$t = \frac{V_2 \cdot \varepsilon \cdot \delta \cdot 60}{F}$$

where

F   = polymer flow rate (g/min)

V_2 = internal volume of the empty pipe (cm^3)

R   = empty pipe radius (mm)

ε = empty volume percent (for Sulzer SMXL models 0.91 to 0.94)

δ = nominal density of the polymer mixture in the melt (about 1.2 g/cm^3)

Not only the mixing of both polymers but also the subsequent spinning of the polymer mixture are carried out at temperatures, depending on the matrix polymer, in a range between 200 and 320° C, preferably at (melt temperature of the matrix polymer + 34) ± 15° C. For PET temperatures are set in the range of preferably 275 to 305°. C.

The production of staple fibers and the filaments, preceding said staple fibers, from the inventive polymer mixtures by spinning at haul-off rates of < 2,500 m/min, preferably 900 to 2,200 m/min, takes place with the use of well-known spinning equipment. In this respect, the prior art filter pack is equipped with filter devices and/or loose filter materials.

After completed shearing and filtration treatment in the spinneret pack, the molten polymer mixture is forced through the holes of the spinneret plate. In the following cooling zone, the melt spun threads are cooled with cooling air to a temperature below their solidification so that adhesion or damming up on the following thread guide member is prevented. The cooling air can be supplied by cross or radial blowing from an air conditioning system or can be taken from the environment by means of its own intake with a cooling pipe. After cooling down, the filaments are injected with spin oil (mixture of water and oil), joined together by means of a thread guide element to form tows, hauled off with a galette system at a defined haul-off rate and coiled into cans by means of a bailing system (e.g. a hank winder).

It is typical for polyester staple fibers that they are produced in large direct melt spinning systems, in which the melt is distributed over long, heated product lines among the individual

spinning lines and inside the lines among the individual spinning systems. In this respect a spinning line represents a stringing together of at least a number of spinning systems, the filaments of which are collected and coiled into tow coiler; and a spinning system represents the smallest spinning unit with a spinning head, which contains a spinneret pack, including a spinneret plate.

In such systems the melt is subjected to high thermal stress during dwell periods of up to 35 minutes. As a consequence of the high thermal stability of the additive, the effectiveness of the polymer additives of the invention does not result in any significant restrictions in increasing the elongation in the filament so that a small quantity of $\leq 2\ \%$ and in many cases of $\leq 1\%$ of the additive to be added suffices despite the high thermal stress. Under the said conditions the result is a uniform polymer mixture, which is characterized surprisingly by a finely dispersed distribution of the additive having a mean particle size of maximum 400 nm and thereby enables good stretchability.

The inventive mixture of polyester and additive allows the spin pump to run preferably at a uniformly high throughput per unit of time, when low fiber titers are to be produced, based on the throughput that is possible when spinning without the polymer additive. Preferably the output rate or the speed of the spin pump is adjusted by a factor f

$$f = \frac{LD_1 \cdot \left(\dfrac{z \cdot C}{100} + VV_1 \right) \cdot v_1}{LD_0 \cdot VV_0 \cdot v_0}$$

higher than when spinning without the addition. In this respect LD is the hole density (n/cm^2) of the spinneret plate; z is a constant ranging from 39 to 153, preferably z is 66 or 146; c is the concentration of the polymer additive in % by wt.; VV is the total draw ratio; and v is the rate of haul-off in m/min, where the indices 1 to 0 relate to the spinning of the matrix polymer without the additive polymer at haul-off rates v_1 or v_0.

According to the invention, an improvement in the stretchability, characterized by a higher draw ratio, is achieved. In particular, if one chooses a suitable additive concentration C, the total draw

ratio VV can be adjusted by at least 0.45 units, in particular to values ≥ 2.9 and in particular preferably to values ≥ 3.5.

In this way the ratio between the discharge and infeed speed in the subsequent fiber drawframe is increased, preferably to at least 2.9. At the same infeed speed a higher production rate of the fiber drawframe is possible.

It has also been demonstrated that the addition of the additive reduces the boiling water shrinkage of the filament. This finding is surprising because in the production of POY yarns with a modifier, the boiling water shrinkage value increases. The explanation lies in the absence of crystallization-influencing effects of the modifier. Even though there is an increase in the elongation of the filament, as in the case of POY yarns, and the overall orientation is reduced, in the production of staple fibers, however, this reduction is achieved totally in the amorphous regions. This special property is especially advantageous for the subsequent stretching in the drawframe. In this respect it is surprising that high efficiency is achieved in the amorphous structural regions at low spinning speeds.

The tows, which are collected in cans, are then further processed into staple fibers in a separate fiber drawframe. The operating parameters of the fiber drawframe are equivalent to those of the state of the art with the exception of the significantly higher total draw ratio of the invention. In detail the fiber drawframe comprises the following steps:

- drawing in at least one step at a temperature, ranging from 20 to 120° C. The total draw ratio VV amounts to at least 2.5.

- optional thermofixing in a dwell period of at least 3 seconds in a temperature range between 80 and 225° C and subsequently cooling down,

- crimping in a stuffer box, during which process the tows can be subjected optionally to a steam atmosphere just before or during the crimping process,

-     drying in a temperature range between 40 and 190° C, and

-     cutting the tow into staple fibers of a mean length ranging from 6 to 220 mm, or collecting the tow in cans and subsequently comminuting into staple fibers. The production rate of the fiber drawframe ranges from 100 to 500 m/min.

The properties of the additive polymer and the mixing technique have the impact that the additive polymer forms bead-like or longitudinally deformed particles in the matrix polymer immediately after the polymer mixture leaves the spinneret. The best conditions were obtained, when the mean particle size (arithmetic mean) was $d_{50} \leq 400$ nm, and the percentage of particles $> 1,000$ nm in a sample cross section was below 1%.

The influence of the draft and/or the drawing on the particles could be proven analytically. New studies on staple fibers, according to the TEM method (transmission electron microscopy), have shown that the conditions for a fibril-like structure are met. The mean diameter of the fibrils was estimated to be approximately 40 nm; and the length-to-diameter ratio of the fibrils was estimated to be > 50. If these fibrils are not formed or if the additive particles are too large after issuing from the spinneret or if the size distribution is too non-uniform, which is the case when the viscosity ratio is inadequate, then the effect of the influence is lost.

Furthermore, for the efficiency of the additives, according to this invention, it is necessary that the glass transition temperature range from 90 to 170° C and that preferably the flow activation energy of the copolymers be at least 80 kJ/mol, thus a higher flow activation energy than that of the polyester matrix. Under this condition it is possible that the additive fibrils solidify before the polyester matrix and absorb a significant percentage of the pending spin tension. The additives that are to be used preferably are also characterized by a high thermostability. Thus, in direct spinning systems that run at a high temperature and/or with a long dwell period the elongation losses due to additive decomposition are minimized.

The staple fibers of the invention exhibit at least the same quality values as staples fibers that are produced analogously without the polymer additive.

The property values in the following examples and in the above text were determined as follows:

Additive fibrils: Thin sections cut in a microtome were examined by means of transmission electron microscopy and then evaluated by means of image analysis. The diameter of the fibrils was assessed; and the length was estimated from the particle diameter, determined on specimens immediately after the spinneret.

The intrinsic viscosity was determined using a solution of 0.5 g of polyester in 100 ml of a mixture comprising phenol and 1,2-dichlorobenzene (3 : 2 parts by weight) at 25° C.

To determine the melt viscosity (starting viscosity), the polymer was dried in a vacuum down to a water content of $\leq$ 1,000 ppm (polyester $\leq$ 50 ppm). Then the granules were put into a cone - plate rheometer, model UM100, Physica Messtechnik GmbH, Stuttgart, DE, while simultaneously blanketing the thermally regulated measurement plate with nitrogen. In so doing, the measurement cone (MK210) was positioned on the measurement plate after melting the specimen, i.e. after approximately 30 seconds. The measurement was started after another heating period of 60 seconds (measurement time = 0 seconds). The measurement temperature was 290° C for polyethylene terephthalate and the additive polymers, which are added to the polyethylene terephthalate, or was equal to the melt temperature of the polyester involved, plus 34.0° C. The measurement temperature, established in this manner, corresponds to the typical processing or spinning temperature of the respective polyester. The quantity of the specimen was chosen in such a manner that the rheometer slot was totally filled. The measurement was carried out in oscillation with a frequency of 2.4 Hz (equivalent to a shear rate of 15 sec^{-1}) and a deformation amplitude of 0.3; and the amount of the complex viscosity was determined as a function of the measurement period. Then the starting viscosity was converted to the zero measurement time by means of linear regression.

To determine the glass transition temperature and the melt temperature of the polyester, the polyester specimen was first melted at 310° C for 1 minute. and then immediately cooled to room temperature. Then the glass transition temperature and the melt temperature were determined by DSC measurement (differential scanning calorimetry) at a heating rate of 10° C/min. Pretreatment and measurement were carried out under a blanket of nitrogen.

The flow activation energy (E) is a measure for the rate of change of the zero viscosity as a function of the change in the measurement temperature. The zero viscosity is the viscosity extrapolated to the shear rate O. The zero viscosity was measured at temperatures in the range between 240 and 280° C with a high pressure capillary rheometer, model Rheograph 2002, Goettfert GmbH, Buchen, DE; and the evaluation was conducted according to the three parameter model of Carreau - Winter. Then the flow activation energy was determined by means of Arrhenius's law from the zero viscosity, according to M. Pahl et al., Praktische Rheologie der Kunststoffe und Elastomere [Practical Rheology of Plastics and Elastomers], VDI Publishers, Dusseldorf (1995), pages 256 ff.

The breaking properties of the filaments were determined with a tensile tester at gauge lengths of 200 mm, a prestressing force of 0.05 cN/dtex and a test rate of 2,000 mm/min.

The boiling water shrinkage of the filaments was determined on specimens, conditioned at room temperature and treated beforehand for 10 minutes in water of $95 \pm 1°$ C.

Reference Example 1:

Polyethylene terephthalate (PET) having an intrinsic viscosity of 0.63 dl/g and a water content of 30 ppm was melted in an extruder at a temperature of 284° C and fed into a product line of the same temperature.

Three SMXL mixers from the firm Sulzer, Switzerland, were installed in the line. The shear rate was 17.5 s^{-1}; and the product, obtained at the shear rate and the 0.8th power of the dwell time in

the mixer (mixer product) in seconds at a polymer throughput of 2,240 g/min, was 483. The melt was spun in a BN 100 spinning system from the firm Zimmer, DE, with circular spinneret and radial quench duct. A hole density of LD = 7.5 cm^{-2} was selected for the spinneret plate. The spin beam temperature was 290° C. The melt spun threads, issuing from the spinneret plate, were cooled with a quantity of 1,400 m^3/h of cooling air, conveyed radially from the outside to the inside, and then finished at a distance of 850 mm from the spinneret plate at a ring oiler, where a water-and-oil mixture was applied, so that the result was a very stable thread state. The spin haul-off rate was 1,350 m/min; and the resulting elongation of the filament was 380%.

Several spin cans were collected and fed to a fiber drawframe. The intake speed was 32 m/min; the drawing was carried out in two steps at 70 and 100° C at a total draw ratio of 3.5. The thermofixing was done in 7 sec. at 220° C; then the tows were cooled down and passed through a stuffer box for crimping. The drying was carried out at 65° C. The staple fibers were produced at a cut length of 38 mm. The titer was 1.14 dtex; the tensile strength was 55 cN/tex, and the elongation at break was 19.3%. The staple fiber production rate was 112 m/min.

The spinning factor yielded 3.7.

Reference Example 2:

By reducing the throughput to 1,748 g/min, a fiber having a titer of 0.89 dtex was produced under otherwise the same spinning conditions, resulting in a spinning factor of 2.9. This draw ratio is too high for this low titer, a problem that manifests itself in the poor stretch development and a significantly reduced elongation at break. In response to the spin elongation of 345%, the VV had to be decreased to 3.3, so that the targeted titer of 0.89 dtex would no longer have been reached. The boiling water shrinkage of the filament was 54%.

Reference Example 3:

In another experiment at a higher speed of 1,850 m/min. the throughput was adjusted in such a manner using a draw ratio of 2.70 that the same titer of 1.14 dtex, which is equivalent to a spinning factor of 3.9, was obtained again as the end product.

The VV of 2.70 was the result of a spin elongation of 270%. Even though the spinning speed was increased by 37%, the SF value increased by only about 6%, because of the digressive behavior of VV at raised spinning speeds. The boiling water shrinkage of the filament was 62%.

Examples 4a - 4c:

The procedure and polyethylene terephthalate (PET) correspond to example 1. However, to produce the polymer mixture according to the invention, a side stream melt system was installed. It comprises an extruder, a dosing pump and an injector. The additive melt was injected directly upstream of the mixer, installed in the polymer line. A copolymer, comprising 91.2 % by wt. of methyl methacrylate with 8.8 % by wt. of styrene, was chosen as the additive, which exhibits a glass transition temperature of 119° C and a PET-based melt viscosity ratio of 4.2 : 1.

The concentration C (% by wt.) was adjusted through a suitable choice of the speed of the dosing pump, based on the polymer throughput.

The polymer throughput was 1,750 g/min. The mixing conditions and the spinning correspond to those of the reference example 2.

The additive concentration and the draw ratio were set to the value in the table. The throughput was increased accordingly, so that the same end titer was obtained. The SF increases, according to the table, with the quantity of additive. The boiling water shrinkage of the filament decreased from 54 to 51%. Due to the increase in the draw ratio according to the table, it was possible to achieve better stretchability. Even the stretching problems in the reference example 2 do not surface.

Example 5:

Examples 4a - 4c were repeated, but the speed was increased to 1,850 m/min, analogously to the procedure in reference example 3; and the additive concentration was adjusted to C = 0.9%. The draw ratio did not have to be changed in relation to the 1,350 m/min setting and did not exhibit the digressive behavior known from unmodified material.

At constant end titer the additive addition yielded an increase in the SF value from SF = 3.9 to 5.1, thus an increase of 31%. With a setting of 1,350 m/min, said addition even yielded an increase from SF = 3.7 to 5.1, thus a 38% increase. The boiling water shrinkage of the filament decreased from 62 to 53%.

Reference example 6 and examples 7 and 8:

The procedure was analogous to that in the above examples, but with polytrimethylene terephthalate (PTT) having an intrinsic viscosity of 0.90 dl/g as the matrix polymer. The additive polymer was the same as in the examples 4a - 4c. The spin beam temperature was 255° C; and the spin haul-off rate was 900 m/min. The drawing was done in two steps at 57 and 70° C; the thermofixing, at 90° C; and the drying, at 70° C. The production rate was 100 m/min. The other parameters are shown in the table.

In all of the examples, according to the invention, the mean diameter of the fibrils in the fibers was below 80 nm.

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Table:

Example no.		1 Reference	2 Reference	3 Reference	4a Invention	4b Invention	4c Invention	5 Invention	6 Reference	7 Invention	8 Invention
Polyester		PET	PET	PET	PET	PET	PET	PET	PTT	PTT	PTT
Additive concentration	%	0	0	0	0.4	0.8	1.5	0.9	0	0.6	1.2
Mixer shear rate γm	sec^{-1}	17.5	13.7	18.5	13.7	15.2	17.5	24.0	19.5	19.5	19.5
Mixer dwell period t	sec	63.3	81.1	59.8	81.0	72.7	63.3	46.1	56.7	56.7	56.7
$\gamma m \cdot t^{0.8}$		483.3	459.9	488.8	460.0	470.1	483.3	514.9	494.0	494.0	494.0
Throughput	g/min	2240	1748	2370	1750	1950	2240	3076	2500	2500	2500
Hole density	$1cm^2$	7.5	7.5	7.5	7.5	7.5	7.5	7.5	6.3	6.3	6.3
Haul-off rate	m/min	1350	1350	1850	1350	1350	1350	1850	900	900	900
Titer	dtex	1.14	0.89	1.14	0.89	0.89	0.89	1.14	3.0	2.6	2.3
Filament elongation at break	%	380	330	270	380	440	540	380	320	390	460
Draw ratio	1:	3.5	3.5	2.7	3.5	3.9	4.5	3.5	3.16	3.6	4.1
Constant K		0.918	0.917	0.919	0.919	0.919	0.914	0.920	0.722	0.738	0.729
Spinning factor SF		3.7	2.9	3.9	2.9	3.2	3.7	5.1	3.9	3.9	3.9

Patent Claims

1.   Polyester staple fibers, characterized in that they comprise

   α)   a polyester, which contains at least 85 Mol-% of poly (C_{2-4}-alkylene) terephthalate,

   β)   0.1 to 2.0 % by wt. of an incompatible, melt processible, amorphous, polymer additive, which exhibits a glass transition temperature ranging from 90 to 170° C, and

   γ)   0 to 5.0 % by wt. of conventional additives

   where the sum of α), β), and γ) is equal to 100%; the ratio of the melt viscosity of the polymer additive β) to the melt viscosity of the polyester component α) ranges from 1:1 to 10:1; and the polymer additive beta) is present in the staple fibers in the form of fibrils, which are distributed in the polyester component alpha) and exhibit a mean diameter of $\leq$ 80 nm.

2.   Polyester staple fibers, as claimed in claim 1, characterized in that the ratio of the melt viscosities ranges from 1.5:1 to 7:1.

3.   Polyester staple fibers, as claimed in claim 1 or 2, characterized in that the polymer additive β) is a copolymer, which contains the following monomer units:

   A =   acrylic acid, methacrylic acid or $CH_2 = CR - COOR'$, where R is an H atom or a CH_3 group, and R' is a C_{1-15}-alkyl group or a C_{5-12}-cycloalkyl group, or a C_{6-14}-aryl group,
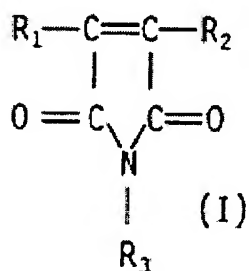
   B =   styrene or C_{1-3}-alkyl-substituted styrenes,

where the copolymer comprises 60 to 98 % by wt. of A and 2 to 40 % by wt. of B, (sum = 100 % by wt.).

4.   Polyester staple fibers, as claimed in claim 3, characterized in that the copolymer comprises 83 to 98 % by wt. of A; and 2 to 17 % by wt. of B (sum = 100 % by wt.).

5.   Polyester staple fibers, as claimed in claim 3 or 4, characterized in that the copolymer comprises 90 to 98 % by wt. of A and 2 to 10 % by wt. of B (sum = 100 % by wt.).

6.   Polyester staple fibers, as claimed in claim 1 or 2, characterized in that the polymer additive β) is a copolymer, which contains the following monomer units:

C =   styrene or C_{1-3}-alkyl-substituted styrenes,

D =   one or more monomers of formula I, II or III

$$R_1-C=C-R_2$$
$$O=C\diagdown_N\diagup C=O$$
$$R_3 \quad (I)$$

$$R_1-C-COOH$$
$$R_2-C-COOH \quad (II)$$

$$R_1-C-C=O$$
$$R_2-C-C=O \diagup O \quad (III)$$
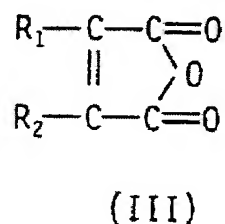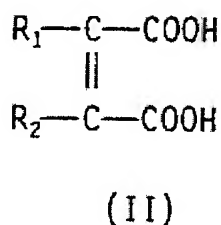
where R_1, R_2 and R_3 are each independently an H atom or a C_{1-15}-alkyl group, or a C_{5-12}-cycloalkyl group or a C_{6-14}-aryl group, and where the copolymer comprises 15 to 95 % by wt. of C and 5 to 85 % by wt. of D, where the sum of C and D together makes 100%.

7.   Polyester staple fibers, as claimed in claim 6, characterized in that the copolymer comprises 50 to 90 % by wt. of C and 10 to 50 % by wt. of D; where the sum of C and D together makes 100%.

8.   Polyester staple fibers, as claimed in claim 6 or 7, characterized in that the copolymer comprises 70 to 85 % by wt. of C and 15 to 30 % by wt. of D, where the sum of C and D together makes 100%.

9.   Polyester staple fibers, as claimed in claim 1 or 2, characterized in that the polymer additive β) is a copolymer, which contains the following monomer units:

E =   acrylic acid, methacrylic acid or $CH_2 = CR - COOR'$, where R is an H atom or a CH_3 group; and R' is a C_{1-15}-alkyl group or a C_{5-12}-cycloalkyl group, or a C_{6-14}-aryl group,

F =   styrene or C_{1-3}-alkyl-substituted styrenes,

G =   one or more monomers of the formula I, II or III
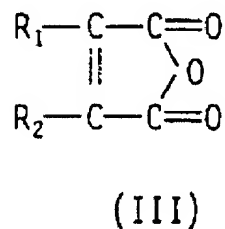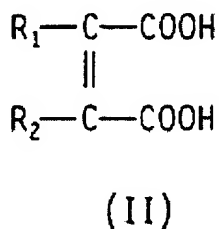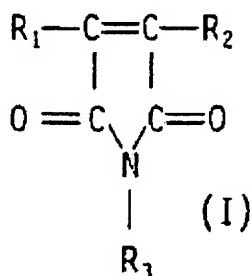
where R_1, R_2 and R_3 are each independently an H atom or a C_{1-15}-alkyl group, or a C_{5-12}-cycloalkyl group or a C_{6-14}-aryl group,

H =   one or more ethylenically unsaturated monomers copolymerizable with E and/or with F and/or with G, selected from the group consisting of alpha-methyl styrene, vinyl acetate, acrylates and methacrylates, which are different from E; vinyl chloride, vinylidene chloride, halogen-substituted styrenes, vinyl ethers, isopropenyl ethers and dienes,

where the copolymer comprises 30 to 99 % by wt. of E; 0 to 50 % by wt. of F; > 0 to 50 % by wt. of G; and 0 to 50 % by wt. of H; where the sum of E, F, G and H together makes 100%.

10. Polyester staple fibers, as claimed in claim 9, characterized in that the copolymer comprises 45 to 97 % by wt. of E, 0 to 30 % by wt. of F, 3 to 40 % by wt. of G and 0 to 30 % by wt. of H; where the sum of E, F, G and H together makes 100%.

11. Polyester staple fibers, as claimed in claim 9 or 10, characterized in that the copolymer comprises 60 to 94 % by wt. of E, 0 to 20 % by wt. of F, 6 to 30 % by wt. of G and 0 to 20 % by wt. of H, where the sum of E, F, G and H together makes 100%.

12. Method for the production of polyester staple fibers, as claimed in any one of the claims 1 to 11, characterized in that

a) a polyester αa), which contains at least 85 Mol-% of poly (C_{2-4} -alkylene) terephthalate, and

0.1 to 2.0 % by wt. of an incompatible, melt processible, amorphous, polymer additive β), which exhibits a glass transition temperature ranging from 90 to 170° C, where the ratio of the melt viscosity of the β) polymer additive to the melt viscosity of the α) polyester component ranges from 1: to 10:1;

where said polyester staple fibers can contain 0 to 5.0 % by wt. of conventional γa) additives,

are mixed in the molten state in a static mixer with shearing, where the shear rate ranges from 12 to 128 sec^{-1}, and the product from the shear rate and the 0.8th power of the dwell time in seconds in the mixer is adjusted to a value of at least 250;

b)   the melt mixture from step a) is spun into filaments, where the spin haul-off rate is below 2,500 m/min;

c)   the filaments from step b) are joined into tows and are drawn, thermofixed, crimped and dried in a separate fiber drawframe, and are cut into staple fibers, where

- the drawing is carried out in at least one step at a temperature ranging from 20 to 120° C and at a total draw ratio VV of at least 2.5,

- the thermofixing is carried out optionally during a dwell period of at least 3 seconds in a temperature range between 80 and 225° C with subsequent cooling,

- the crimping is carried out in a stuffer box, during which process the tows can be subjected optionally to a steam atmosphere just before or during the crimping process,

- the drying is carried out in a temperature range between 40 and 190° C, and

- the cutting into staple fibers of a mean length ranging from 6 to 220 mm, or the curling of the tow into cans and the subsequent comminution into staple fibers is carried out at a production rate of the fiber drawframe ranging from 100 to 500 m/min.

13.   Method for the production of polyester staple fibers, as claimed in claim 12, characterized in that the throughput per unit of time in step b) while spinning at the haul-off rate v_1 is adjusted by a factor f

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$$f = \frac{LD_1 \cdot \left(\dfrac{z \cdot C}{100} + VV_1 \right) \cdot v_1}{LD_0 \cdot VV_0 \cdot v_0}$$

higher than in relation to spinning the polyester component α) without the polymer additive β at the haul-off rate v_0,

where: $LD_{0/1}$ is the hole density (n/cm^2) of the spinneret plate;

         C   is the concentration of the polymer additive in % by wt.,

         $VV_{0/1}$ is the total draw ratio without the additive at the respective spin haul-off rate v_0 or v_1,

         $v_{0/1}$ is the spin haul-off rate in m/min, and

         z   is between 39 and 153.

14.   Method for the production of polyester staple fibers, as claimed in claim 12 or 13, characterized in that the concentration C of the polymer additive ranges from 0.1 to 2.0 % by wt. according to

$$C = \frac{(VV - VV_0)}{z} \cdot 100\%$$

where VV or VV_0 is the draw ratio with or without the additive addition and $VV \geq VV_0 + 0.153$.

15.   Method for the production of polyester staple fibers, as claimed in claim 13 or 14, characterized in that z is between 66 and 146 and $(VV - VV_0) \geq 0.45$.

16.   Method for the production of polyester staple fibers, as claimed in any one of the claims 12 to 15, characterized in that the staple fibers exhibit a titer ranging from 0.5 to 4.0 dtex; the spin haul-off rate ranges from 900 to 2,200 m/min, and the concentration C of the polymer additive is selected in the range between 0.1 and 2.0 % by wt. according to

$$C = \frac{(R_d - R_{do})}{B},$$

where b is between 80 and 160; R_d is the desired elongation at break in % of the inventive filament; R_{do} is the elongation at break in % of the filament without the additive addition; and R_d is $\geq$ 370%, when R_{do} is $\leq$ 354%.

17.   Method for the production of polyester staple fibers, as claimed in claim 16, characterized in that b is between 115 and 152.

(12) INTERNATIONAL APPLICATION PUBLISHED PURSUANT TO THE PATENT COOPERATION TREATY

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(54) Title: POLYESTER STAPLE FIBERS AND METHOD FOR THE PRODUCTION THEREOF

(57) Abstract: Polyester staple fibers consisting of a polyester, 0.1 to 2.0 w.- % of an incompatible, melt processable, amorphous polymeric additive with a glass transition temperature of 90 to 170 °C and a melt viscosity/polyester component ratio of 1:1 to 10:1, and 0 to 5.0 weight % of usual additives. The polymeric additives in the staple fibers are present in the form of fibrils with a mean diameter of ≤ 80 nm. The invention also relates to method for the production of staple fibers, comprising mixing and simultaneously shearing the polyesters and the polymeric additives and optionally the usual additives and spinning at a speed of < 2500 m/min relative to form of spun fibers. Said are bundled together to form cables and stretched in aseparate drawframe to form separate reels of fiber, crimped, dried and cut to form staple fibers.

/English and German international search report/

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